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Original Article

The Cause of Whitening by Flame Retardants Treatment on Korean Wooden Cultural Heritage[1]

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ABSTRACT

Korean wooden cultural heritages are treated by flame retardants to protect fire hazards. Two types of flame retardants are used to treat wooden cultural heritage. These flame retardants cause some problems such as surface whitening, discoloration, and cracks due to the chemical reaction caused by Korean traditional wood painting (Dancheong), flame retardant and wood humidity. The Korean government is trying to cut down on the amount of flame retardants for the wooden cultural heritage because of these problems. This study was carried out to find the cause of whitening by flame retardants treatment. The reaction between pigment and flame retardant chemicals was analyzed by infrared spectroscopy.

Keywords : wooden cultural heritage, white stain, Korea traditional paint, analysis

1. INTRODUCTION

Wooden cultural heritages are being damaged by natural and anthropogenic disasters such as fire, earthquake, biological and anthropogenic damages (Back and Lee, 2006; Cha *et al*., 2011). Among the damage, the damage caused by fire is about seventy times over the last 12 years in Korea. The fire makes the serious damage to the wooden cultural heritage compared to other disaster factors (Phillip *et al*., 2005; Kim *et al*., 2012; Park *et al*., 2013).

Most of wooden cultural heritages of Korea are located in the mountains. Wooden buildings in the mountain are vulnerable to fire due to the lack of management and narrow forest roads. There are two methods for protecting wooden cultural heritages. First method is applying a flame retardant on the surface of wooden cultural heritages. Secondary, it is to install fire prevention equipment inside of cultural heritages (Cha *et al*., 2011; Park *et al*.,

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2013). But because of the institutional and budget problem, the coating method using flame retardants is usually applied (California Building Standards Commission, 2010).

The flame retardants for wooden cultural heritages in Korea have several problems such as whiteness of building surface and absorption moisture. Because of these problems, it was interrupted to process the flame retardant on the traditional paint "Dancheong" treated on wooden cultural heritages buildings (Park *et al*., 2013; Lee *et al*., 2015).

This study was carried out to investigate the chemical reaction effect between the flame retardants on the wooden cultural heritage and Korean traditional paints 'Dancheong'.

2. MATERIALS and METHODS

2.1. Materials

2.1.1. Flame retardants

There are two types of flame retardants registered at Korean Cultural Heritage Administration. Flame retardants are applied to wooden cultural heritage surface by spraying method. The appearances are transparent and colorless. The company does not disclose the composition of the flame retardants. Types of flame retardants were classified with flame retardant-A (FR-A) and flame retardant-B (FR-B).

2.1.2. Pigment

The wooden cultural heritages in Korea were coated by the traditional paint for the beauty of the building. The traditional paint is composed of various pigments for the color expression. Table 1 shows the pigment materials used in the test.

Table 1. Materials used in the sample production

Name	Chemical formula
Oyster shell white	$CaCo_3$
Iron oxide red	Fe_2O_3
Lead red	$PbCrO_4$
Cyanine green colony	$C_{32}Cl_{16}CuN_8$
Titanium dioxide	TiO_2
Chrome oxide green	Cr_2O_3
Ultramarine blue	$Na_6Al_6Si_6O_{24}S_4$
Iron oxide yellow	$Fea_2O_3 \cdot H_2O$
Permanent orange G	$C_{32}H_{24}C_{12}N_8O_2$
Cobalt blue	$CoA_{l2}O_4$
Permanent yellow	$C_{18}H_{18}N_4O_6$
Emerald green	$Cu(OOCCH_3)_2 \cdot 3CuO(AsO_2)_2$
Toluidine red	$C_{17}H_{13}N_3O_3$
Chrome yellow	$PbCrO_4$

2.2. Methods

For the reaction of the flame retardants and pigments, the 0.3 g of pigments were placed in conical flask of 50 mℓ capacity with 10 mℓ flame retardants, allowed to stand for 24 hours after shaking. Samples were treated for 15 minutes at 5000 rpm in a centrifuge after lapse of 24 hours to separate pigments and flame retardants. The pigments were centrifuged by 5000 rpm filled with 500 mℓ of distilled water separated from compositions of pigments and flame retardants two times. The pigments dried in temperature 100℃ for 3 hours for analyse. The control groups were centrifuged in the same way as above, however, distilled

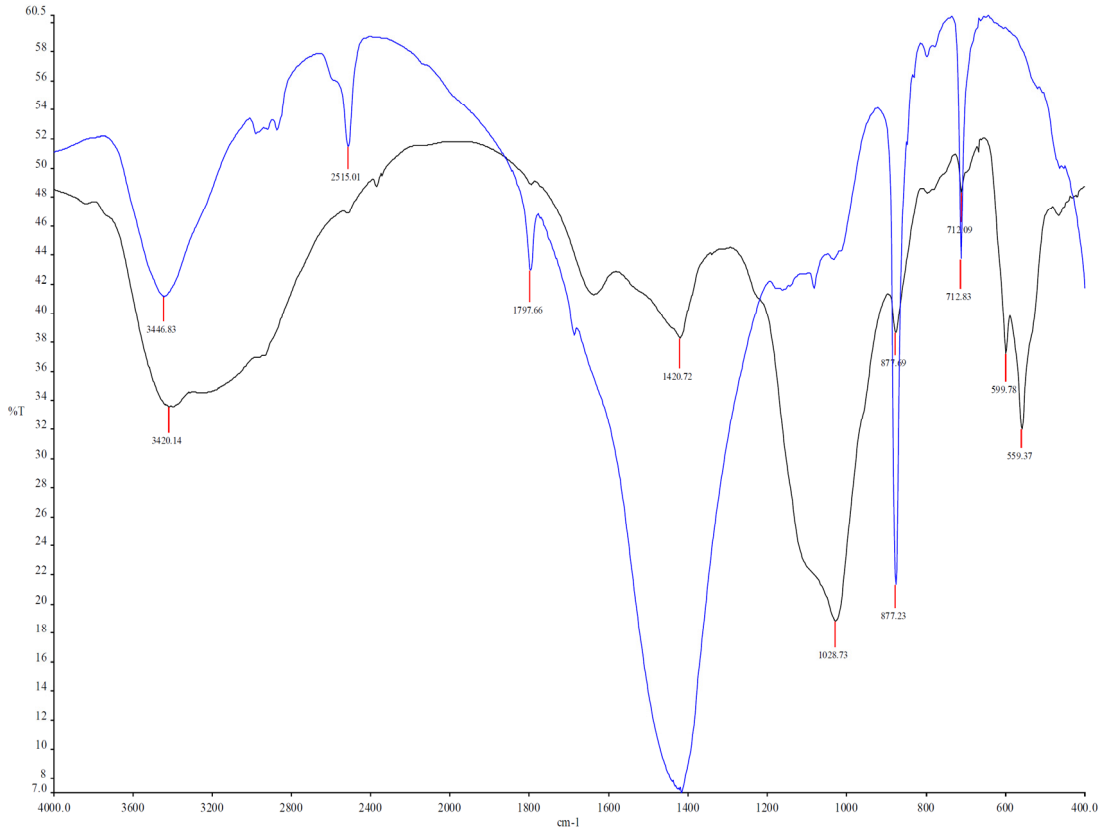

Fig. 1. Oyster shell white: FR-A (Black line)/Control Group (Blue line).

water was used instead of flame retardants.

2.2.1. FT-IR spectroscopy

The spectrum of the analysis sample was measured by Spectrum GX (Perkin Elmer Spectrum GX FT-IR, Perkin Elmer Inc., USA). The spectrums were measured at Mid-IR single source, 4000～400 cm^{-1} range condition.

2.2.2. X-ray fluorescence

X-ray fluorescence analysis was conducted with ZSX PrimesII (XRF, Rigaku, North America). The analysis sample was measured upper surface, then stepped down to 4 kV. All experiments were conducted at room temperature.

3. RESULTS and DISCUSSION

3.1. The reaction of the FR-A and pigments

The Fig. 1 shows the FT-IR spectrums of the reactants which are formed by flame retardants A (FR-A) with oyster shell white reaction. There are significant difference between the FR-A and control. It is due to triethanolamine

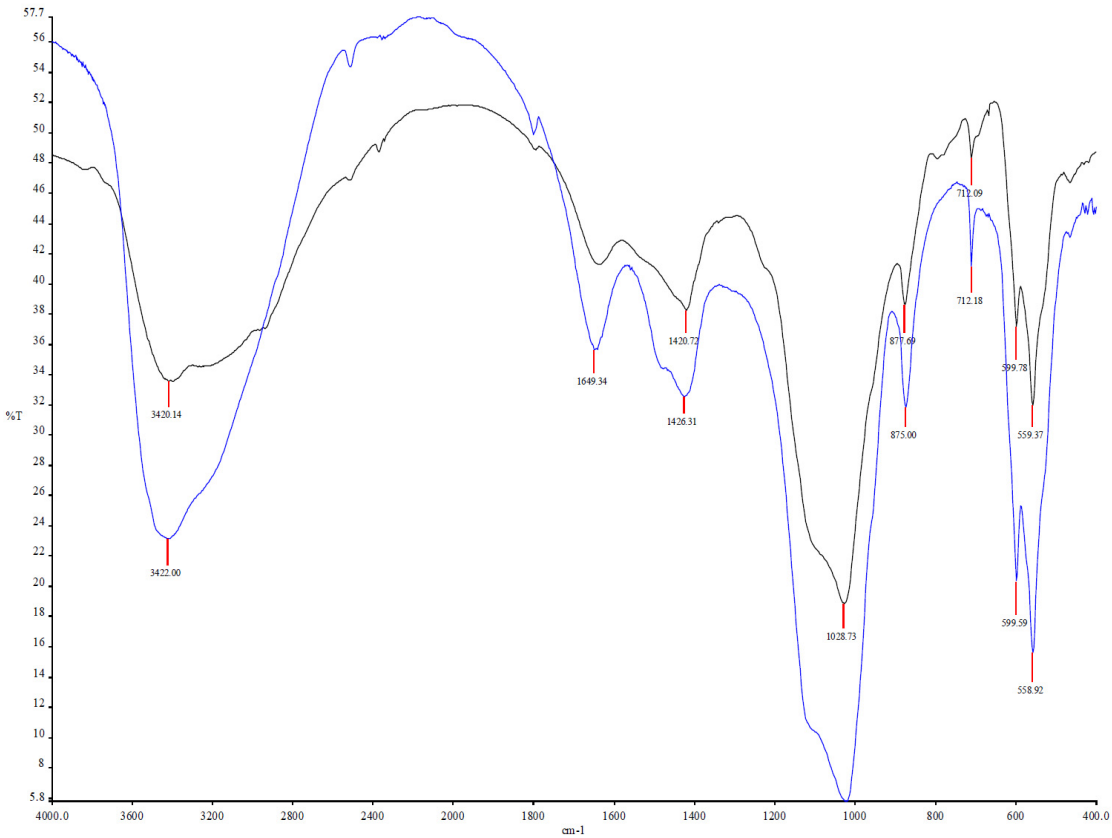

Fig. 2. Compare FR-A reaction product (Black line) and Calcium Phosphate Tribasic ($Ca_3(PO_4)_2$) (Blue line).

phosphate [$C_6H_{15}NO_3 \cdot H_3PO_4$], which contained FR-A, is formed to tricalcium phosphate [$Ca_3(PO_4)_2$] for the following chemical reaction.

$$2[C_6H_{15}NO_3 \cdot H_3PO_4] + 3CaCO_3 \rightarrow Ca_3(PO_4)_2 + 2[C_6H_{15}NO_3] + CO_2 \uparrow$$

Fig. 2 shows that FR-A reactants and tricalcium phosphate are in consistency.

Fig. 3 shows that the reactant of FR-A and lead red. This graph shows the peak of the reactant 1056 cm^{-1} and 987 cm^{-1}, and it is different compared with that of control. It is due to triethanolamine phosphate [$C_6H_{15}NO_3 \cdot H_3PO_4$] of FR-A, which formed to lead phosphate [$Pb_3(PO_4)_2$] for the following chemical reaction.

$$2[C_6H_{15}NO_3 \cdot H_3PO_4] + Pb_3O_4 \rightarrow Pb_3(PO_4)_2 + 2[C_6H_{15}NO_3]$$

Through the analysis of the flame retardants and pigments, it was confirmed that the oyster shell white and lead react with FR-A. And they were formed to tricalcium phosphate and triethanolamine phosphate. Also, it confirmed that the other pigments did not react with FR-A.

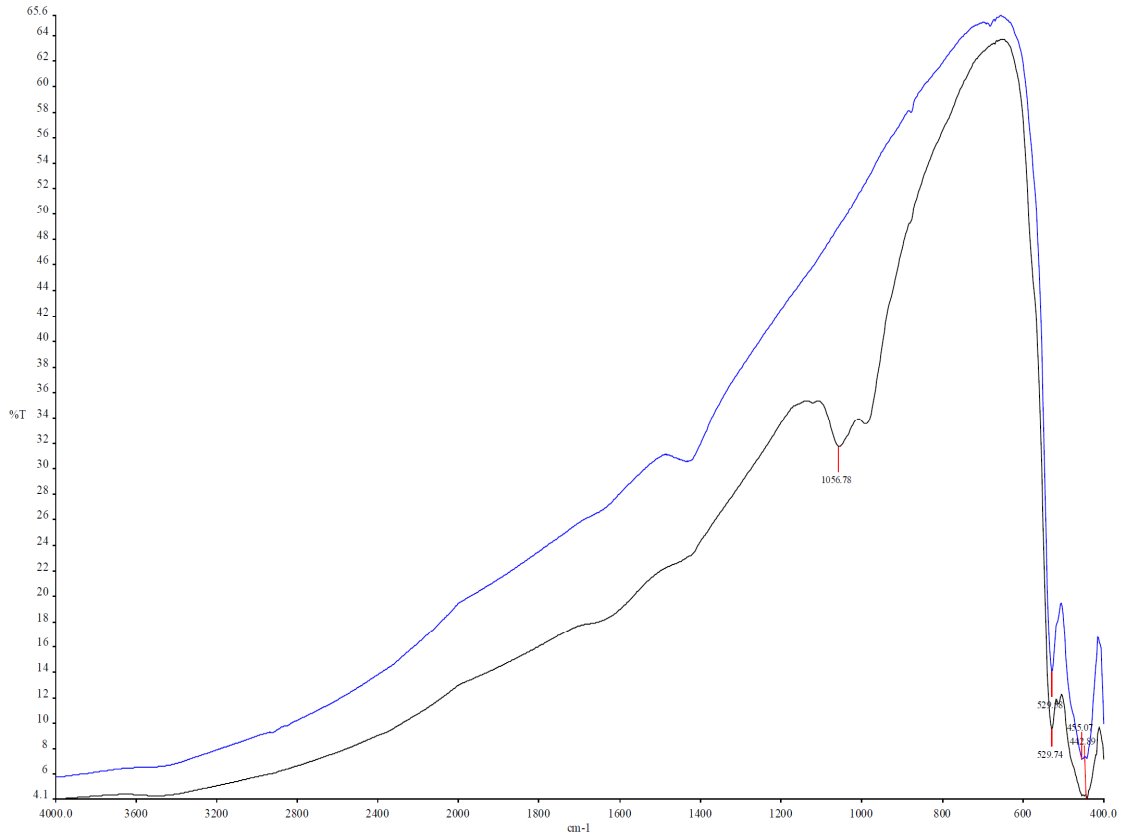

Fig. 3. Lead red: FR-A (Black line)/Control Group (Blue line).

3.2. The reaction of the FR-B and pigments

FR-B did not form reaction products in the reaction process of FR-A methods. The reaction sample of the FR-B was obtained in the following methods. The mixtures by prepared with oyster shell white 2.00 g and FR-B 20.0 g were centrifuged on 5000 rpm, 15 min to separate liquid and solid after 24 hour. The blending chemical specimens were dried at room temperature for three days. The white solids were obtained by separating from the mixtures of paste and methanol after the mixtures were dried at 100℃. Fig. 4 shows the FT-IR spectrum of white solid. Also, Table 2 shows the result of XRF analysis of white solid.

The major components of the white solid are P (54.0%) and Ca (39.7%) as shown in the Table 1. The white solid was decided ATMP-Ca salt (Fig. 5) which has N $[CH_2PO(OH)_2]3 \cdot xCa$ structure produced by FR-B main component of ATMP-NH_4 reacted 'oyster shell white' following formula.

$$N[CH_2PO(OH)_2]_3 \cdot xNH_4 + xCaCO_3 \rightarrow N[CH_2PO(OH)_2]_3 \cdot xCa + CO_2 \uparrow$$

Table 2. FR-B and Oyster Shell White reaction of XRF result (unit: wt.%)

Na	Mg	P	S	K	Ca
0.377	0.208	54.0	0.198	1.87	39.7
Mn	**Fe**	**Ni**	**Cu**	**Br**	**Sr**
0.059	0.510	0.015	0.015	2.92	0.075

* Na: Natrium / P: Phosphorus / S: Sulfur / K: Potassium / Ca: Calcium
Mn: Manganese / Fe: Iron / Ni: Nickel / Cu: Cuprum / Br: Bromine / Sr: Strontium

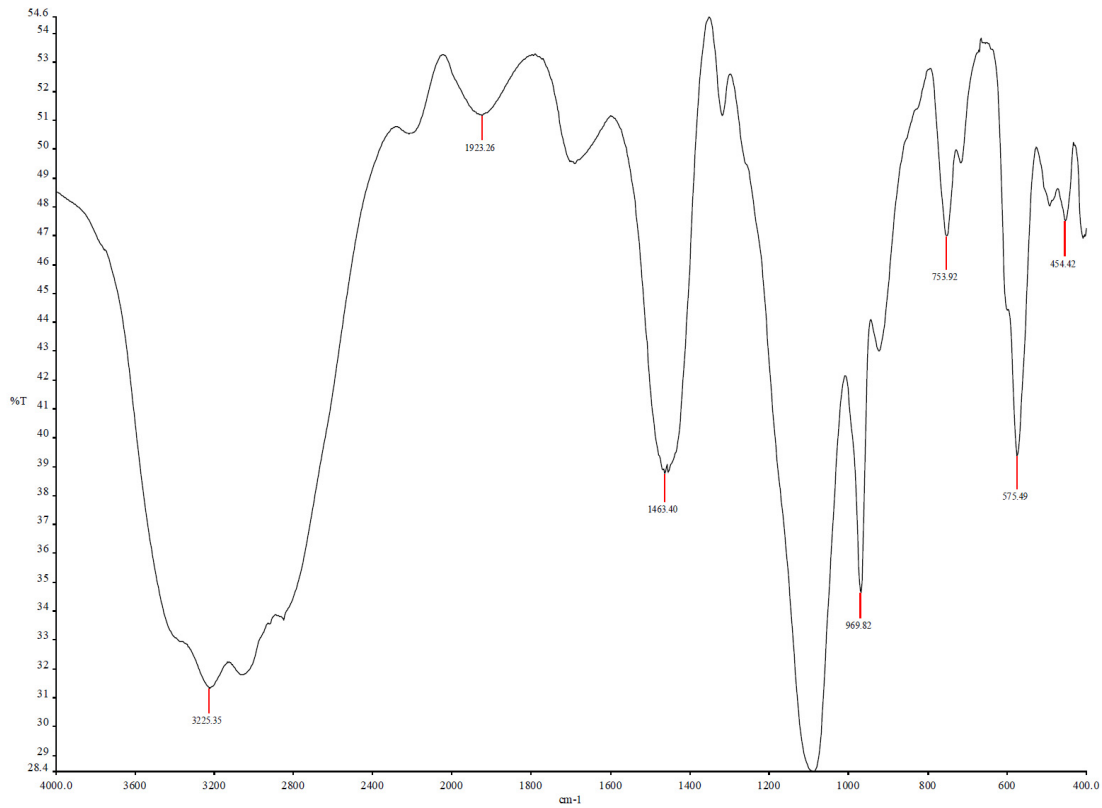

Fig. 4. FR-B and Oyster Shell White reaction of infrared spectrum.

The pigment 'Permanent orange G' occurred transparent solid in the same method as 'Oyster shell white'. Fig. 6 and Table 3 shows the result of IR and XRF analyses.

The main component of transparent solid was P (27.0%) and Pb (71.2%) (Table 2). The spectrum of Fig. 6 is similar to that of ATMP-Ca

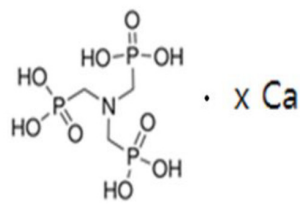

Fig. 5. ATMP-Ca salt.

Table 3. FR-B and Permanent orange G reaction of XRF result (unit: wt.%)

Al	P	S	K
0.247	27.0	0.361	0.038
Ca	**Fe**	**Zn**	**Pb**
0.074	0.067	1.03	71.2

* Al: Aluminum / P: Phosphorus / S: Sulfur / K: Potassium
Ca: Calcium / Fe: Iron / Zn: Zinc / Pb: Plumbum

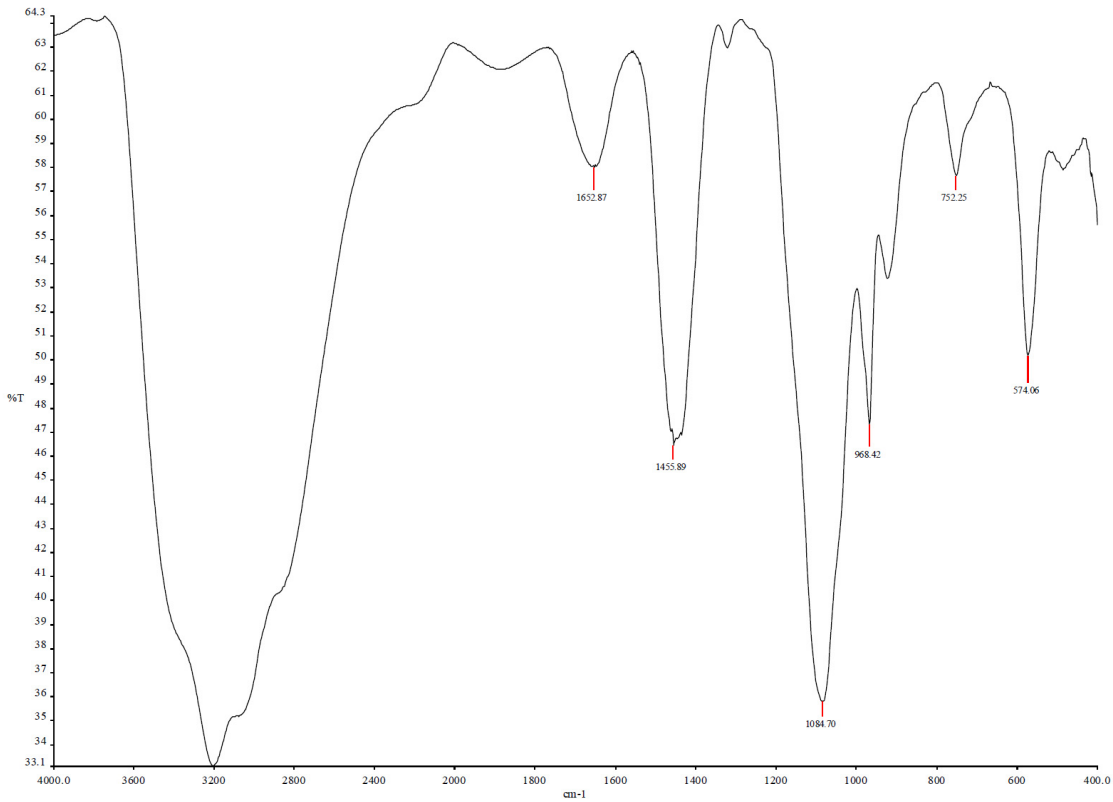

Fig. 6. FR-B and Permanent orange G reaction infrared spectrum.

salt. It could be concluded that transparent solid is ATMP-Pb salt. 100 mg of chrome yellow ($PbCrO_4$) was mixed with FR-B 10.0 g. The reaction mixture, which was prepared by 24 hours, was separated at 5000 rpm for 15 minutes. The green paste was generated in the supernatant liquid, which was dried at room temperature for three days. The Fig. 7 shows the result of IR analysis.

Table 4 shows the result of XRF analysis.

The main components of the green paste are P (10.5%), Cl (ch (0.304%), Cr (0.191%) and Pb (0.330%) (Table 4). First, P is main component of FR-B. And Cl is generated in the proc-

Table 4. FR-B and Chrome yellow reaction of XRF result (unit: wt.%)

Na	Al	Si	P	Cl	K	Ti
0.0792	0.0273	0.0047	10.5	0.304	0.0012	trace
Cr	**Fe**	**Ni**	**Br**	**Rb**	**Pb**	**C**
0.191	0.0013	0.0009	0.0029	0.0009	0.330	88.5

* Na: Natrium / Al: Aluminum / Si: Silicon / P: Phosphorus / K: Potassium / Ti: Titanium
Cr: Chromium / Fe: Iron / Ni: Nickel / Br: Bromine / Rb: Rubidium / Pb: Plumbum / C: Carbon

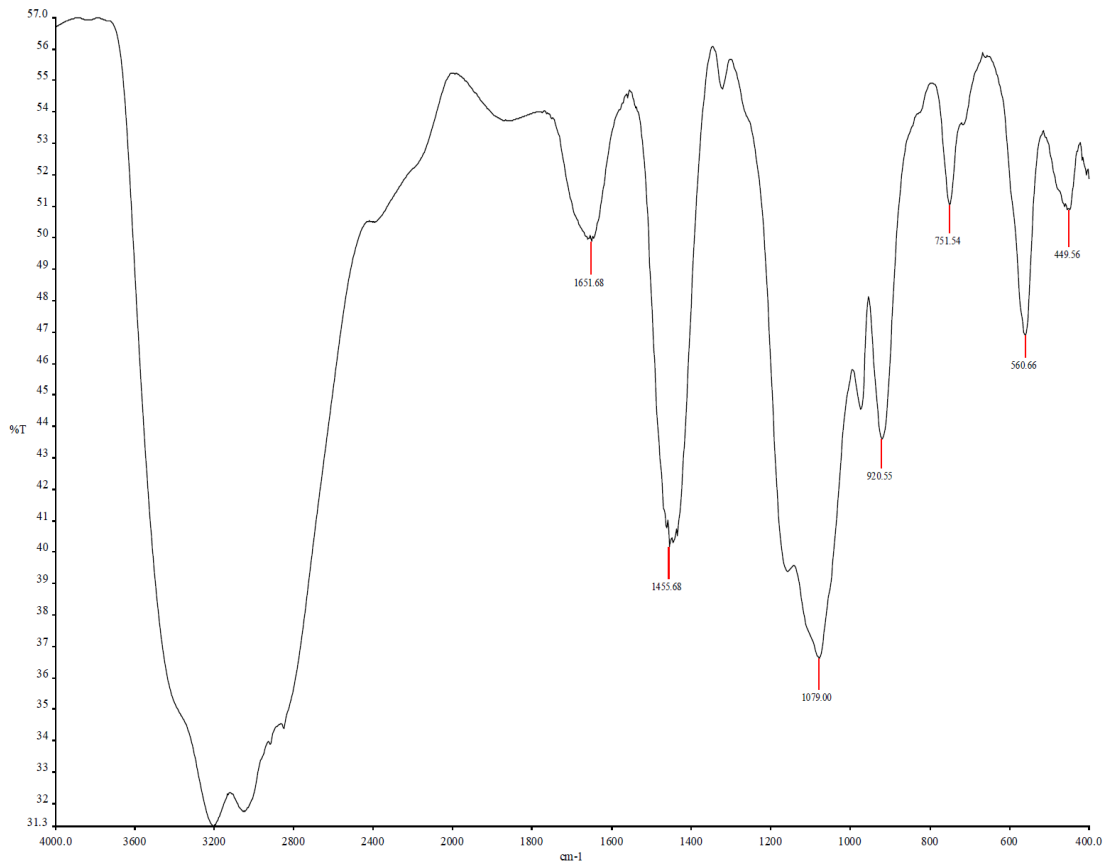

Fig. 7. FR-B and Chrome yellow reaction infrared spectrum.

ess of synthesis of ATMP. Also, Cr and Pb are components of Chrome yellow ($PbCrO_4$). It was confirmed in the course of chrome yellow dissolving by measuring that elements. So the color of liquid was change to dark green. 100 mg of ultramarine blue ($Na_6xAl_6xSi_6 + xO_{24}NaySz$) was mixed with FR-B 10.0 g. The reaction mixture, which was prepared by 1 week, was separated at 5000 rpm for 15 minutes.

The solid changed the color to grey from ultramarin blue's blue color. The Fig. 8 and 9 show the results of IR analysis. And Table 4

Table 5. Ultramarine blue and FR-B reaction's XRF result (unit: wt.%)

	Na	Mg	Al	Si	P	S	Cl
Ultramarine blue	13.7	0.097	19.0	37.0	0.122	25.9	0.115
Reactant	0.220	0.0483	6.36	55.4	0.445	34.4	-
	K	**Ca**	**Ti**	**Cr**	**Mn**	**Fe**	**Ni**
Ultramarine blue	1.53	0.183	0.658	trace	0.007	1.07	0.013
Reactant	0.560	0.0775	1.29	-	-	0.711	0.012
	Cu	**Ga**	**Rb**	**Sr**	**Y**	**Mo**	**Ba**
Ultramarine blue	0.0042	0.0042	0.019	0.0484	0.0289	0.0338	0.0811
Reactant	0.0093	-	-	0.0246	-	-	0.105

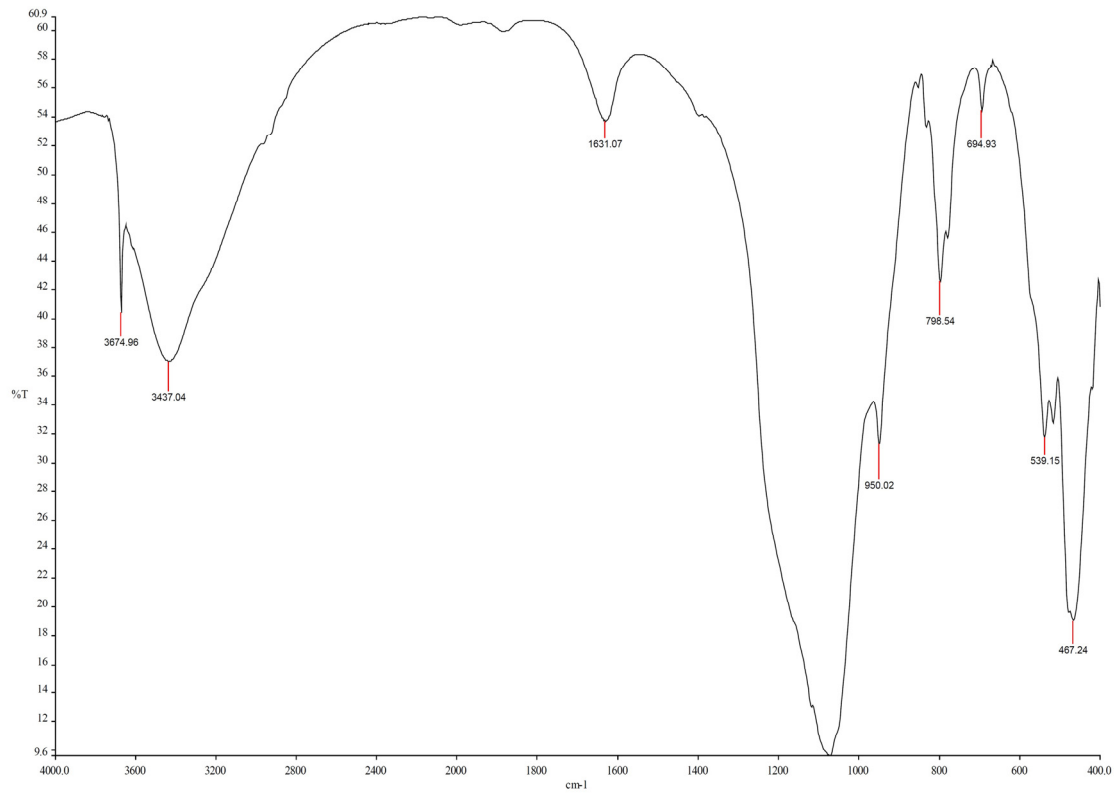

Fig. 8. FR-B and Ultramarine blue reaction supernatant's infrared spectrum

shows the results of XRF analysis. The reactant of FR-B and ultramarine blue show different IR spectra (Fig. 8 and 9). However, the reactant of Na shows a tendency to decrease percentage amount from 13.7% to 0.220%. Al also shows that the percentage amount decreases from 19.0% to 6.36% after the reaction. Table 5 shows the results referred to above. It is de-

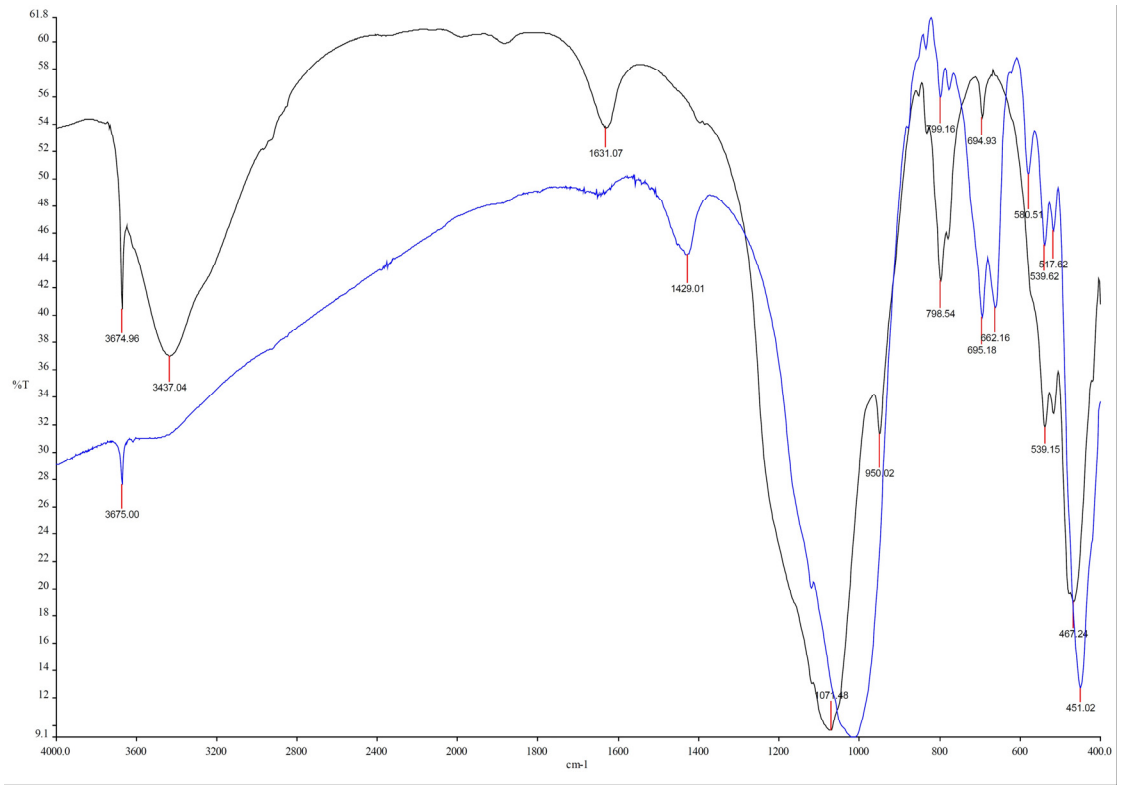

Fig. 9. FR-B reaction product and Ultramarine blue's comparative infrared spectrum

termined that the components of Na and Al of the ultramarine blue are detected as FR-B was dissolved. So the color of liquid was changed to grey.

4. CONCLUSION

This study was carried out to investigate the effect of the flame retardant of wooden cultural heritage. The following conclusion was obtained from this study. At first, some pigments were able to produce crystal materials by reacting pigments with flame retardants. Calcium carbonate in Oyster Shell White reacted with triethanolamine phosphate, which were contained of FR-A, they were converted to tricalcium phosphate. Secondly, the reactants were also confirmed to cause changes in the colorant. The solid materials were changed to grey color from ultramarin blue to blue color. Also, it is determined that the components of Na and Al of the ultramarine blue are detected as the FR-B is dissolved. It resulted in a color change of the liquid to grey. In conclusion, the flame retardants used in wooden cultural heritage should be modified to avoid the traditional painting problem.

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